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(21) Application number : 2001-348552 (71) Applicant : TAIHEIYO CEMENT CORP
(22) Date of filing : 14.11.2001 (72) Inventor : NAKANISHI HIROSHI
ISHIMORI MASAKI
TSUKADA KAZUHISA
YAMADA KAZUO

(54) WATER-HARDENABLE COMPOSITION

(57) Abstract:

PROBLEM TO BE SOLVED: To provide a water-hardenable composition containing iron sulfate, cement and a polycarboxylic acid based polymer compound.

SOLUTION: The water-hardenable composition is excellent in the effect for preventing elution of hexavalent chromium, can maintain appropriate fluidity for a fixed term in its kneaded material after water is added, is excellent in workability in the construction field, such as application properties, form placing properties and the like, and is provided with excellent strength developing properties and fluidity maintaining properties without generating excess setting retardation.

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CLAIMS

[Claim(s)]

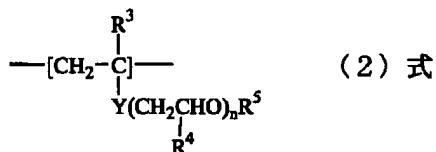
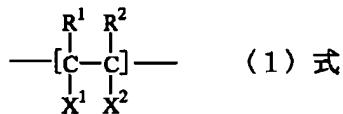
[Claim 1]A hydraulic composition containing ferrous sulfate, cement, and a polycarboxylic acid system high molecular compound.

[Claim 2]The hydraulic composition according to claim 1 which is 0.05 - 5 weight-section **** thing to cement 100 weight section about ferrous sulfate.

[Claim 3]The hydraulic composition according to claim 1 or 2 whose ferrous sulfate is ferrous sulfate anhydrous salt, ferrous sulfate monohydrate, ferrous sulfate 4 monohydrate, ferrous sulfate 5 monohydrate, or ferrous sulfate 7 monohydrate.

[Claim 4]A hydraulic composition of Claims 1-3 whose polycarboxylic acid system high molecular compound is what has a structural unit expressed with following the (1) type and (2) types to intramolecular given in any 1 clause.

[Chemical formula 1]



(R1 - R4 are the same or different among a formula, a hydrogen atom, a methyl group, or an ethyl group is shown, X1 shows a hydrogen atom, a methyl group, or -(CH₂)_mCOOM₁, and X2 shows -COOM₁.) M₁ shows a hydrogen atom, an alkaline metal, alkaline-earth metals, ammonium, or organic amine, and m shows an integer of 0-2. R₅ shows an alkyl group of the carbon numbers 1-3, Y shows -CH₂O- or -COO-, and n shows an integer of 5-300.

[Claim 5]The hydraulic composition according to claim 4 whose content of a structural unit which constitutes a polycarboxylic acid system high molecular compound is (1) type / (2) formula =10-1 in monomer mol terms.

[Claim 6]A hydraulic composition of Claims 1-5 whose weight average molecular weight of a polycarboxylic acid system high molecular compound is 2000-200000 in polyethylene-glycol conversion given in any 1 clause.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention does not have elution of hexavalent chromium, and relates to the good hydraulic composition of dispersibility.

[0002]

[Description of the Prior Art]About 1% and calcium sulfate (gypsum fibrosum) are contained in cement for sulfuric acid alkali, such as sodium sulfate and potassium sulfate, about about 1 to 3% as sulfate from the former. These originate in a cement raw material, or are added for hydration activity

adjustment of a cement composition mineral of C3A. However, it is expected that a variety, various wastes, etc. will be used for a cement raw material from a viewpoint of effective use of global environmental protection or resources from now on, and sulfuric acid alkali and the increase in content of C3A (reduction in SM of cement) are expected in cement, and if spread, it leads also to the increase in the amount of addition gypsum fibrosum. The increase in the content of heavy metals can be considered as a cause of concern. When most heavy metals use cement, it is fixed in the hydrate of cement and it is supposed that there is no increase of the load to environment, but about chromium, it begins to melt in part as hexavalent chromium into a solution, and the elution volume exceeding environmental standards may be shown. As an elution reducing method of this chromium (6 values), the method by the reduction to trivalent chromium from harmful hexavalent chromium by ferrous sulfate, etc. are shown. However, we are anxious about the increase in the sulfate ion concentration in the liquid phase, and the increase in these sulfuric acid alkali and gypsum fibrosum and addition of the ferrous sulfate as an environmental measure have a possibility that this may cause the fall of the dispersibility at the time of polycarboxylic acid system water reducing agent addition.

[0003]

[Problem to be solved by the invention] However, in the cement composition containing these ferrous sulfate, when the conventional water reducing agent was added by the increase in the sulfate ion concentration in the liquid phase, it became clear that the problem that dispersibility falls arises. Therefore, the purpose of this invention is to provide the good cement composition of dispersibility, containing ferrous sulfate.

[0004]

[Means for solving problem] Then, as a result of examining many things, when blending with cement combining ferrous sulfate and a polycarboxylic acid system high molecular compound, this invention person finds out that the hydraulic composition with which the elution preventive effect and the outstanding dispersibility of hexavalent chromium by the reducing action of ferrous sulfate were compatible is obtained, and came to complete this invention.

[0005] That is, this invention provides the hydraulic composition containing ferrous sulfate, cement, and a polycarboxylic acid system high molecular compound.

[0006]

[Mode for carrying out the invention] The ferrous sulfate used for the hydraulic composition of this invention acts as a reducing agent of hexavalent chromium, and the anhydrous salt of ferrous sulfate, monohydrate, four monohydrates, five monohydrates, and seven monohydrates are mentioned. The ferrous sulfate concerned receives cement 100 weight section from a point of the reduction effect in this invention constituent -- 0.05 to 5 weight section -- especially -- 0.1 - the amount part of duplexs -- further -- it is preferred to carry out 0.2-1.5 weight-section content. In less than 0.05 weight sections, ferrous sulfate will reduce the dispersibility of a polycarboxylic acid system water reducing agent, if an effect is scarce and exceeds five weight sections as a reducing agent of hexavalent chromium, it can consider the influence of the coagulation on a hydraulic composition, and high cost-ization by superfluous addition further, and is not preferred.

[0007] As cement, CaO and 3Al₂O₃ (C3A), What is necessary is just one sort or a thing included two or more sorts about one mineral components of CaO and 3SiO₂ (C3S), CaO and 2SiO₂ (C2S), and CaO, 4Al₂O₃ and Fe₂O₃ (C4AF). As a raw material for offering each ingredient of C3A, C3S, C2S, and C4AF, publicly known raw materials for cement production, such as limestone, argillite, and fly ash, can use, and various wastes, such as various burned ash and sewage-sludge dry powder, can also be used as a raw material.

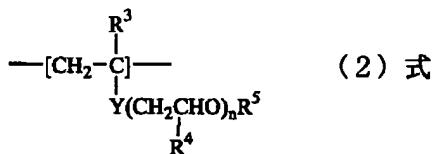
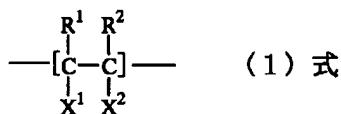
[0008] Other sulfate, for example, sulfuric acid alkali, and gypsum fibrosum may be suitably included in a hydraulic composition of this invention as adjustment of a raw material situation or hydration activity.

[0009] As for these ferrous sulfate and cement components, preparing as ferrous sulfate content cement is preferred. For example, said cement raw material is calcinated at 1000-1500 ** with a rotary kiln etc., clinker is produced, gypsum fibrosum and ferrous sulfate are added to a clinker grinding thing which ground and obtained this, and a hydraulic substance is produced. Although neither a clinker grinding method nor the degree of crushed grain in particular is limited, but it may be the same in general with being carried out by general cement production, for example, gypsum fibrosum and ferrous sulfate are added in a clinker grinding thing, Especially as gypsum fibrosum used by this invention, it is not limited, for example, anhydrous gypsum, hemihydrate gypsum, and gypsum dihydrate can be mentioned, as adjustment of hydration activity, the content is a range which can carry out adequate amount addition suitably, and its complement is preferred to hydration activity adjustment of C3A. When manufacturing cement, even if it adds gypsum fibrosum and ferrous sulfate in a clinker grinding thing, simultaneous adding of gypsum fibrosum and the ferrous sulfate may be carried out at the time of clinker grinding, and cement may be produced.

[0010] What has a structural unit expressed with the following (1) type and (2) types to intramolecular as a polycarboxylic acid system high molecular compound is preferred.

[0011]

[Chemical formula 2]



[0012] (R1 - R4 are the same or different among a formula, a hydrogen atom, a methyl group, or an ethyl group is shown, X1 shows a hydrogen atom, a methyl group, or $-(\text{CH}_2)_m\text{COOM}_1$, and X2 shows $-\text{COOM}_1$.) M1 shows a hydrogen atom, an alkaline metal, alkaline-earth metals, ammonium, or organic amine, and m shows the integer of 0-2. R5 shows the alkyl group of the carbon numbers 1-3, Y shows $-\text{CH}_2\text{O}-$ or $-\text{COO}-$, and n shows the integer of 5-300.

[0013] It is preferred that the content of the structural unit which constitutes a polycarboxylic acid system high molecular compound is (1) type / (2) formula =10-1 in monomer mole-ratio conversion. This is for foaming stability and dispersibility to fall that a fluid fall becomes large with it being size, and it is less than one from (1) type / (2) type =10.

[0014] As for the weight average molecular weight of this polycarboxylic acid system high molecular compound, it is preferred that it is 2000-200000 in polyethylene-glycol conversion. If weight average molecular weight exceeds less than 2000 and 200000, since dispersibility falls, neither is preferred.

[0015] As for this polycarboxylic acid system high molecular compound, what contains 0.05 to 3 weight section more preferably 0.01 to 5 weight section by solid content conversion to cement component 100 weight sections, such as C3A in a hydraulic composition, is good. Since it may have an adverse effect on coagulation retardation or the intensity manifestation nature after hardening in the combination in which the loadings of less than 0.01 weight sections are not enough as an effect, and it exceeds five weight sections with them, it is not desirable.

[0016] The publicly known retarder generally used for the cement composition can be used for this invention, For example, hydroxy acid, the salt and keto acid,

the salt and aminocarboxylic acid, publicly known organic system retarders, such as the salt, sugars, and sugar-alcohol, and publicly known inorganic system retarders, such as a silicofluoride, boric acid, phosphoric acid, a zinc compound, a lead compound, and a copper compound, are mentioned. Although this retarder may be mixed and used for a polycarboxylic acid system high molecular compound and it may add independently, when workability is taken into consideration, it is more preferred to mix and add to a polycarboxylic acid system high molecular compound.

[0017]A hydraulic composition of this invention can be added to said polycarboxylic acid system high molecular compound, and can contain suitably cement admixture, such as publicly known admixture an object for cement, and for concretes and/or limestone, slag, and fly ash.

[0018]If it is publicly known aggregate currently used for usual concrete, mortar, etc. as aggregate, anything can be included in a hydraulic composition of this invention. Although river sand, an inland sand, crushed sand, a crushed stone, silica sand of natural aggregate and a lightweight aggregate, etc. are preferred especially as such publicly known aggregate, fly ash, slag, rinsed beach sand, calcium carbonate, etc. can also be used for others. Loadings of aggregate are 100 to 700 weight section preferably [in the case of 30 to 1000 weight section, and concrete] to hydraulic composition (ferrous sulfate and cement) 100 weight section. In less than 30 weight sections, a shrinkage amount of a hardening constituent increases, there is concern of generating, such as a crack, and it is not desirable. If 1000 weight sections are exceeded, mobility at the time of water addition and a fall of cured body intensity are caused, and it is not desirable.

[0019]A hydraulic composition of this invention is a thing which blended water and which also contains a mixture of a moisture state in general. As for loadings of water, it is preferred to consider it as 20 to 100 weight section to cement forming component 100 weight sections, such as C3A contained in a hydraulic composition. Although mulling is desirable in the case of water addition, since this hydraulic composition does not harden after a mull stop immediately, but a good flow state is maintained for a while, construction etc. can be performed between them.

[0020]

[Working example]Although an embodiment is given and this invention is explained concretely hereafter, this invention is not limited to this.

[0021]After calcinating mixtures, such as Embodiments 1-6 and the comparative example 1, 2 limestone powder, clay, aluminum ash, and iron powder, at about 1400 **, Mineral components of Table 1 which ground and set Blaine's specific surface area to 3800 cm²/g in an included clinker grinding thing Hemihydrate gypsum, Ferrous sulfate anhydrous salt was added and two kinds of cement compositions (A, B) of chemical composition which carried out choke crushing of this and showed Blaine's specific surface area in Table 2 of 4300 cm²/g were manufactured. To this cement composition, as a fine aggregate An inland sand of 5 mm of maximum droplet sizes, As an about 25% of solids concentration solution and an object for comparison of a high molecular compound (1-3) which carried out copolymerization of the monomer of mol composition ratio (a blending ratio is mol %) furthermore shown in Table 3, and obtained it. A commercial dispersing agent (naphthalene sulfonic acid formalin condensate;N) and water were mulled for 3 minutes in a Hobert mixer by combination shown in Table 4, and a hydraulic composition was produced. A mortar flow value 60 minutes after immediately after a mull of a produced hydraulic composition and compressive strength of a mortar test piece using this hydraulic composition were measured by a method based on JIS 5201. The result is shown in Table 7.

[0022]

[Table 1]

セメント種	構成成分	C3S	C2S	C3A	C4AF
C-A	クリンカー中の含有重量%	59	19	8	9
C-B	クリンカー中の含有重量%	49	14	12	13

[0023]

[Table 2]

セメント種	化学成分	Ig. loss	Insol	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	R ₂ O
C-A	重量%	1.8	0.2	20.8	5.2	2.8	64.0	1.3	2.1	0.62
C-B	重量%	1.3	0.1	18.0	7.0	4.2	60.8	2.1	3.8	0.45

表中Rはアルカリ金属を示す。

[0024]

[Table 3]

共重合体種(高分子化合物)		(1)	(2)	(3)
使用单量体種		配合モル%	配合モル%	配合モル%
a)	メタクリル酸	59	50	
	無水マレイン酸			64
b)	MEメタクリル酸エステル(n=40)		21	8
	MEメタクリル酸エステル(n=23)	14		
c)	メタクリルスルホン酸ナトリウム	17	13	15
d)	アクリル酸メチル		16	
	メタクリル酸エチル	10		13
共重合体重量平均分子量		40500	48000	32000
a)/b)の单量体モル比		4.2	2.4	8.0

表中MEは、メトキシポリオキシエチレンを表している。

[0025]

[Table 4]

	使用セメント	使用高分子化合物	配合量(g)			
			セメント	細骨材	水	高分子化合物
実施例1	C-A	(1)	500	1100	225	4.0
実施例2	C-A	(2)	500	1100	225	3.5
実施例3	C-A	(3)	500	1100	225	3.8
実施例4	C-B	(1)	500	1100	225	4.5
実施例5	C-B	(2)	500	1100	225	4.0
実施例6	C-B	(3)	500	1100	225	4.3
比較例1	C-A	N	500	1100	225	7.0
比較例2	C-B	N	500	1100	225	8.5

注) 使用高分子化合物(N)は、ナフタレンスルホン酸ホルマリン縮合物である市販

分散剤。

[0026]

[Table 5]

	モルタルフロー値 (mm)				圧縮強さ (N/mm ²)
	直後	15分	30分	60分	
実施例1	195	193	190	187	43.5
実施例2	192	190	185	180	44.5
実施例3	195	198	202	194	42.7
実施例4	192	189	182	178	43.0
実施例5	196	187	181	175	44.1
実施例6	194	197	190	183	42.1
比較例1	175	160	148	137	38.6
比較例2	155	138	113	107	37.8

[0027] To said cement composition, as an inland sand and coarse aggregate as a fine aggregate The crushed stone of about 200 mm of maximum droplet sizes, After mixing and mulling a commercial dispersing agent (N) and water by a compulsive biaxial type mixer as the about 25% of solids concentration solution and the object for comparison of a high molecular compound (1-3) which carried out copolymerization of the monomer of the mol composition ratio (a blending ratio is mol %) shown in said table 3, and obtained it so that it may become loadings given in Table 6, The slump immediately after a mull and after 60-minute progress was measured by the method according to JIS A1101. The pillar mold with a 10-cm height [in diameter] of 20 cm was filled up with kneaded material, and the compressive strength of the molded product unmolded and obtained in 24 hours was measured. A result is shown in Table 7.

[0028]

[Table 6]

	使用セメント	使用高分子化合物	配合量 (kg)			
			セメント	細骨材+粗骨材	水	高分子化合物
実施例1	C-A	(1)	20	84	9	0.16
実施例2	C-A	(2)	20	84	9	0.14
実施例3	C-A	(3)	20	84	9	0.15
実施例4	C-B	(1)	20	84	9	0.19
実施例5	C-B	(2)	20	84	9	0.155
実施例6	C-B	(3)	20	84	9	0.17
比較例1	C-A	N	20	84	9	0.35
比較例2	C-B	N	20	84	9	0.45

注) 使用高分子化合物 (N) は、ナフタレンスルホン酸ホルマリン結合物である市販分散剤。

[0029]

[Table 7]

	スランプ (cm)		圧縮強度 (N/mm ²)
	直後	60分	
実施例1	18.5	17.5	19.0
実施例2	19.5	17.0	18.8
実施例3	18.5	18.0	18.4
実施例4	18.8	17.5	18.2
実施例5	19.0	17.2	17.6
実施例6	19.2	17.5	17.8
比較例1	18.0	12.5	16.3
比較例2	14.8	6.5	15.8

[0030] With the hydraulic composition contained so much, ferrous sulfate so that clearly from Table 5 and 7. When naphthalene sulfonic acid formalin condensate is

used as a water reducing agent, since dispersibility falls, a mortar flow value and a slump index fall, the fixed time maintenance of the moderate mobility cannot be carried out, but it turns out that field-work nature, such as workability and mold restoration nature, is bad. On the other hand, when a polycarboxylic acid system high molecular compound is used for the hydraulic composition which contains ferrous sulfate so much as a water reducing agent. Since dispersibility is good, and a mortar flow value and a slump index do not fall but fixed time mobility is maintained, it turns out that it excels in field-work nature, such as workability and mold restoration nature.

[0031]

[Effect of the Invention]The hydraulic composition of this invention has the extremely outstanding intensity manifestation nature and flow holdout, without excelling in a hexavalent chromium elution preventive effect, and being able to carry out fixed time maintenance of the moderate mobility in the kneaded material after water addition, excelling in field-work nature, such as workability and mold restoration nature, and causing excessive coagulation retardation.